INTERLABORATORY STUDY 92-5

PHENOLICS (4-AAP) IN REAGENT WATER AND SURFACE WATER

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INTERLABORATORY STUDY 92-5
PHENOLICS (4-AAP) IN REAGENT WATER AND SURFACE WATER

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TABLE OF CONTENTS

1. SUMMARY . . . . Page 2

2. TECHNICAL OUTLINE . . . . Page 4

2.1 SAMPLE PREPARATION . . . . Page 4

2.2 PROCEDURE . . . . Page 4

2.3 DISTRIBUTION . . . . Page 5

2.4 DATA HANDLING . . . . Page 5

3. RESULTS AND DISCUSSION . . . . Page 6

3.1 REAGENT WATER SAMPLES . . . . Page 6

3.1.1 Phenol Samples . . . . Page 6

3.1.1 Acetic Acid Sample . . . . Page 11

3.1.2 Resorcinol Sample . . . . Page 15

3.2 HAMILTON HARBOUR WATER SAMPLES . . . . Page 16

3.3 SUMMARY OF STUDY FINDINGS . . . . Page 18

4. BIBLIOGRAPHY . . . . Page 19

5. APPENDIX . . . . Page 20

I. EVALUATION METHODOLOGY . . . . Page 20

I.1 Summary of The Two-Sample Performance Evaluation Procedure . . . . Page 20

I.2 Limits for Maximum Interlaboratory Repeatability and Reproducibility . . . Page 22

I.3 Two Sample Plot Discussion . . . . Page 24

II RAW DATA . . . . Page 25

III LIST OF PARTICIPANTS . . . . Page 26

1. SUMMARY

This is the third interlaboratory study initiated as part of an ongoing program of the Quality Management Office (QMO), Laboratory Services Branch (LSB) of the Ontario Ministry of the Environment (MOE) to evaluate the ability of laboratories to measure Phenolics in reagent water and other matrices.

In the previous two MOE studies (89-6, 91-3), the samples were spiked with reagent Phenol (C_6H_5OH) and the participants were required to analyze them using the 4-AAP method[1,2]. Only a third of the participants in both studies demonstrated acceptable performance. The term 'acceptable' throughout these studies is based on a factor times the estimated average repeatability of the participants.

This study (92-5) was initiated to evaluate the ability of laboratories to analyze samples containing a higher homolog of Phenol such as Resorcinol ($m\text{-}C_6H_4(OH)_2$), and samples containing volatile acids such as Acetic Acid.

Forty-five laboratories initially agreed to participate in the present study. Two laboratories failed to report results after receiving the samples.

Eight samples, five in reagent water and three in Hamilton Harbour water (see table 2.1) were prepared by the QMO and distributed to the participants. The participants were requested to analyze the samples using the 4-AAP method specified in the MISA (Municipal and Industrial Strategy for Abatement) regulations[3].

The results as they were received were entered into a Lotus 123® spreadsheet. A hard-copy of the electronic spread sheet was sent to all participants for verification.

The performance of the participants was evaluated using the King-Selliah[4,5] graphical procedure.

A comparative summary of findings for the three studies (in reagent water samples) is presented in Table 1.1

The findings of these three studies are essentially the same. The average recovery and the repeatability estimates of the three studies are not significantly different. In the present study about half of the participants were capable of producing valid analytical data in simple matrices such as reagent water containing reagent Phenol (C_6H_5OH). Nine laboratories have shown improvement in this study compared to the previous studies. This demonstrates the positive impact of repeated interlaboratory studies on data quality.

TABLE 1.1

SUMMARY OF STUDY FINDINGS

	STUDY 92-5		STUDY 91-3	STUDY 89-6
Matrix	DDW	HHW	DDW	DDW
# of labs received samples	45	45	40	30
# of labs reported results	43	43	38	30
Acceptable performance (within warning limits)	20 (46.5%)	15 (34.9%)	12 (31.6%)	10 (33%)
Exceeded warning limits but within control limits	4 (9.3%)	8 (18.6%)	4 (10.5%)	4 (13%)
Out of control/Erratic	8 (18.6%)	4 (9.3%)	7 (18.4%)	4 (13%)
Low bias	6 (14.0%)	6 (14.0%)	9 (23.6%)	9 (30%)
High bias	4 (9.3%)	8 (18.6%)	6 (15.8%)	3 (10%)
Slope dependant bias	3 (7.0%)	7 (16.3%)	4 (10.5%)	3 (10%)
Intercept dependant bias	6 (14.0%)	7 (16.3%)	3 (7.9%)	6 (20%)
Other	1 (2.3%)	2(4.6%)		
Repeatability (S_w)	.86 µg/L*		.89 µg/L	.86 µg/L

* pooled   DDW = Deionized distilled water   HHW = Hamilton Harbour water

The majority of laboratories had a similar outcome in both matrices. This includes thirteen laboratories that were assessed as acceptable performers in both matrices. Twenty laboratories (46.5%) were within control limits in both matrices.

The majority of laboratories did not recover Resorcinol. The 4-AAP method was not intended to measure all Phenolic compounds present in the sample, but rather provide a minimum estimate of Phenolic compounds present[7]. Presence of compounds such as Resorcinol are not likely to bias the results of the majority of laboratories.

The presence of volatile acids in the sample too are not likely to cause a positive bias for the majority of the laboratories. However for laboratories using buffers with insufficient buffer capacity, samples containing volatile acids may present problems. This study suggests that a Borax\Sodium Potassium Tartrate buffer system is most appropriate for 4-AAP analysis of Phenolic compounds.

This study suggests that differences in distillation conditions (temperature, rate etc.) and buffer systems introduce biases, even among otherwise reliable laboratories, when analyzing samples containing higher homologs of Phenol or volatile acids. Standardized distillation conditions and buffer systems are recommended if consistency of data is to be achieved.

2. TECHNICAL OUTLINE

2.1 SAMPLE PREPARATION

2.1.1 REAGENTS

i) Deionized Distilled Water (DDW)

ii) Homogenized Hamilton Harbour Water (HHW)

Hamilton Harbour water was collected from the intake pipe at the Hamilton Dofasco plant on July 8, 1992. The water was thoroughly mixed and filtered before usage.

iii) MOE Phenol Standard, Lot# PHEN01 (10 mg/L)

iv) MOE Phenol Standard, Lot# PHEN02 (10 mg/L)

v) Resorcinol Standard.
Dissolved 0.1003 g of Resorcinol (Baker analyzed) in 500 mL of DDW

vi) Glacial Acetic Acid, Analar grade

2.1.2 PROCEDURE

30 L of each type of sample (listed in Table 2.1) was prepared. In each case 18 L (3 x 6 L) of the matrix was quantitatively transferred to a clean stainless steel tank. A fourth portion of 6 L matrix containing appropriate amounts of spiking standards (Table 2.1) was added to the tank. This was followed by the last 6 L portion of the matrix. The contents of the tank were mixed thoroughly for 15 minutes using a mechanical stirrer.

Approximately 250 mL of this bulk solution was immediately dispensed into appropriately labelled special 250 mL 'Phenol' bottles containing about 2 mL of 50% Sulphuric Acid as preservative.

TABLE 2.1
Spiking chart for sample preparation

SAMPLE	Phenol STD. PHENO1	Phenol STD PHENO2	RESOR-CINOL STD	ACETIC ACID	MATRIX
D11	-	-	-	-	Reagent water
D12	30 mL	30 mL	-	-	Reagent water
D13	30 mL	90 mL	-	-	Reagent water
D14	-	-	300 mL	-	Reagent water
D15	-	-	-	30 mL	Reagent water
H11	-	-	-	-	Hamilton Harbour water
H12	30 mL	30 mL	-	-	Hamilton Harbour water
H13	30 mL	90 mL	-	-	Hamilton Harbour water

2.2 DISTRIBUTION

Prior to sample preparation, the participating laboratories received a letter of notification. The laboratories confirmed their willingness to participate in this study by letter or telephone. The participants were also requested to answer a questionnaire pertaining to their analytical methodology. Each participant was assigned a laboratory identification code. These codes are different from those assigned in the previous MOE Phenol studies. A list of participating laboratories is included in the Appendix (section 5.III).

A total of eight samples were packaged in cardboard boxes and were shipped to most participants via Purolator courier on July 28, 1992. A few samples were hand delivered. No sample losses in transit were reported. Included with the samples were result reporting forms.

2.3 DATA HANDLING

The majority of the laboratories utilized the result reporting forms to submit their findings to the QMO. All data were manually entered by laboratory code into an electronic spreadsheet.

Tables of results were sent to all participants for verification on September 9, 1992. The participants were requested to report any transcription errors before September 18, 1992. One laboratory identified a transcription error. The database was corrected accordingly.

3. RESULTS AND DISCUSSION

Forty five laboratories received a total of eight samples, five in reagent water and three in Hamilton Harbour water. The composition of these samples are summarized in Table 2.1 (page 5). Forty three participants reported results for all samples. Two laboratories did not report any results.

The data was evaluated by the King-Selliah[4,5] graphical procedure. An outline of this automated procedure is given in the Appendix (5.I.1).

Based on the standard deviations of the 'selected laboratories' (i.e. after rejecting outliers), the evaluation is performed either on an absolute scale (concentration units) or on a relative scale (as percentage of target or median). The former will result in a rectangular graph and the latter will result in a square graph. In this study the evaluation was performed on an absolute scale.

Warning and control limits have been used as the basis to flag laboratories that did not demonstrate acceptable repeatability or reproducibility. The term 'acceptable' throughout this evaluation is based on an estimate of average repeatability of all participants (excluding those too far from the 45 degree axis).

The K-S procedure allows data to be evaluated with respect to study median or expected value. In this instance the targets were known and hence the data was evaluated with respect to expected values.

3.1 REAGENT WATER SAMPLES.

3.1.1 Phenol Samples

Forty three laboratories reported results for these samples. Among these, sixteen participated in the previous studies[1,2] (89-6, 91-3).

The sample D11 was the unspiked reagent water. As expected, the majority of the laboratories reported 'not measurable' (i.e. results were typically <2 µg/L) for this sample.

Samples D12 & D13 were reagent water spiked with different amounts of reagent Phenol (C_6H_5OH). The results of these two samples were treated by the K-S procedure to evaluate proficiency of individual laboratories to measure Phenols in simple matrices.

Sample D14 and D15, containing Resorcinol ($m\text{-}C_6H_4(OH)_2$) and Acetic Acid, respectively were used to evaluate an individual laboratory's efficacy to measure higher homologs of Phenol and its capability to measure Phenolics in general in the presence of volatile acids. The results of these two samples are discussed later.

Comparative summaries of the outcomes of K-S procedure of the three studies are presented in Tables 1.1, 3.1 & 3.2. Table 3.1 is the statistical summary of all three studies. The repeatability (S_w) indicated in this table represents the average within-laboratory standard deviation estimated based on the results of each study as described in the Appendix (section 5.I.1).

TABLE 3.1

STATISTICAL SUMMARY

	STUDY 92-5				STUDY 91-3		STUDY 89-6*	
SAMPLE	D12	D13	H12	H13	D2	D3	PHN 2	PHN 3
Target (µg/L)	20	40	20	40	20	40	10	40
ALL LABORATORIES								
# of Labs	42	42	41	41	38	38	30	30
Mean (µg/L)	19.9	39.3	20.2	39.1	18.3	48.2	9.7	50
Median (µg/L)	20	40	21	40.2	19.0	40	8.9	39
AFTER ELIMINATING OUTLIERS								
# of Labs	38	41	40	36	26	29	20	23
Mean (µg/L)	19.3	39.6	20.6	39.8	18.3	39.2	8.8	39
Median (µg/L)	20	40	20.75	40	18.8	40	9.9	39
S (µg/L)	2.15	3.01	2.88	3.18	1.88	3.25	1.9	2.0
Average recovery (median/ target x 100)	100%	100%	103.75%	100%	94%	100%	99%	97.5%
Repeat-ability S_w (µg/L)	0.86				.89		0.86	

* RESULTS OF STUDY 89-6 WERE REPORTED IN MG/L. THEY WERE CONVERTED TO µG/L IN THE ABOVE TABLE.

Table 3.2 presents the outcome of evaluations of individual laboratories in this study identified by the 92-5 laboratory codes. The results of laboratories that also participated in the previous studies are presented on the same row.

The key to this table is as follows:

A	Acceptable performance
ER	Both results erratic
H	Biased high
He	Biased high and/or erratic
Hi	Biased high, possible intercept problem
HI	Biased high, probable intercept problem
Hs	Biased high, possible slope problem
HS	Biased high, probable slope problem
IS	Insufficient sensitivity
Le	Biased low and/or erratic
Li	Biased low, possible intercept problem
LI	Biased low, probable intercept problem
Ls	Biased low, possible slope problem
LS	Biased low, probable slope problem
ND	Not detected
OC	Out of control-one result erratic
WAI	Warning: slight imprecision
WHI	Warning: Biased high, probable intercept problem
WHS	Warning: Biased high, probable slope problem
WLS	Warning: Biased low, probable slope problem
WLi	Warning: Biased low, possible intercept problem
WLI	Warning: Biased low, probable intercept problem
WOC	Warning: Out of control-one result erratic

TABLE 3.2
SUMMARY OF LABORATORY PERFORMANCE

CODE	92-5		91-3	89-6
Matrix	DDW	HHW	DDW	DDW
3101	LI	LI	WLi	
3102	LS	Ls	LS	OC
3103	A	A	A	A
3104				LS
3105	A	A	A	A
3106	IS	IS	Hs	
3107	WOC	A		
3108	A	A	LS	OC
3109	A	A	A	A
3110	A	HI		
3111	HS	HI		
3112	Li	LS	WLi	LI
3113	OC	OC	OC	
3114				
3115	OC	OC	LI	LS
3116	A	A	A	LI
3117	He	He	ER	Li
3118	LI	WLS	A	A
3119	OC	A	OC	
3120	LI	Ls		
3121	OC	OC	Le	OC
3122	A	A		A
3123	ER	H	He	
3124	A	WAI	A	
3125	A	A	WLi	
3126	He	OC		
3127	ER	LS		
3128	A	A	LI	A
3129	A	WHS		
3130	WOC	WAI	A	
3131	HI	HI		
3132	A	A		WAI
3133	ER	He		
3134	A	HI		
3135	A	A	A	
3136	OC	WLS	Hi	A
3137	A	WHI		
3138	A	ND	Le	Ls
3139	WOC	WHI		
3140	A	A	He	ER
3141	A	WOC	ER	
3142	LI	Le		
3143	A	A	A	A
3144	A	A	H	
3145	WHS	He		

FIGURE 3.1

SAMPLE D12 VS D13

REAGENT WATER

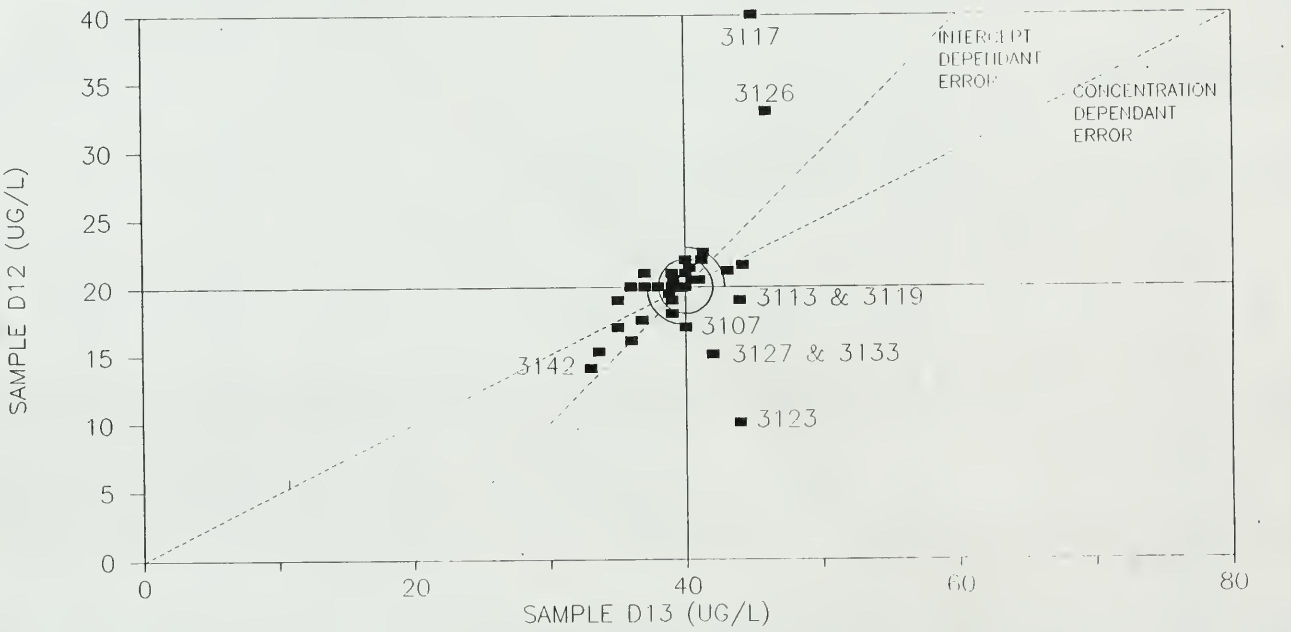


Figure 3.1 (page 10) is the graphical presentation of the findings of the present study. Each point represents a pair of results from each participant. Some of the laboratories that have exceeded the warning limits have been identified. A detailed explanation of the two sample plots are given in the Appendix (section 5.I).

The average recovery and the repeatability estimates of all three studies are not significantly different.

20 laboratories (46.5%) in the present study demonstrated acceptable performance. These laboratories can be considered as capable of producing valid analytical data in simple matrices such as reagent water. Another 4 (total of 24; 56%) produced results that were within control limits. This is a considerable improvement from the previous studies.

Nine laboratories that were flagged as not meeting the requirements of acceptable performance in the previous studies have demonstrated acceptable performance in the present study. This improvement in the performance of these individual laboratories is very encouraging.

Only one laboratory has shown deterioration in performance compared to the previous studies.

Concentration dependant biases (slope biases) appear to be the major problem for three laboratories in the present study. Such biases are caused by either inaccurate standards or inadequate calibration procedures. Use of certified reference standards or use of the same source of 'quality' external standards by all laboratories will probably improve the data comparability.

Six laboratories demonstrated intercept dependant bias. Such biases are caused by inappropriate base-line and/or background and/or blank correction. In automated continuous flow systems the 'wash' water used between samples may be contaminated with low levels of Phenols. This would lead to lower results.

Eight laboratories in this study were flagged as erratic or out of control. These eight laboratories must achieve greater control over the entire analytical system before a diagnosis of biases is possible.

3.1.1 Acetic Acid Sample

The MOE analysts have recognized that the 4-AAP method for measuring Phenolics is very sensitive to pH changes[6]. Under certain pH conditions, 4-AAP tends to undergo self-condensation to yield a coloured complex which could easily be mistaken for a 'Phenol response'. Therefore a buffer is always used to minimize pH changes during the colour development and measurement process.

Since some 'real samples' may contain volatile acids that will distil over along with Phenolics and potentially alter the pH, the buffer used must be of sufficient capacity to resist any changes in pH. In addition an 'acid' is released in the 4-AAP method. Inappropriate selection of buffer or inadequate buffer strength may permit the pH to shift from the desired pH range.

Sample D15 was spiked with copious amounts of Acetic acid to test the relative adequacy of the buffer system used by different laboratories. It will introduce a positive response if the buffer system is inadequate. Ideally there should be 'no response' for this sample as it contains no Phenolics. Because of the large amounts of acid used, any reading of 10 µg/L (as Total Phenol) or less is considered satisfactory.

TABLE 3.3
SUMMARY OF LABORATORY PERFORMANCE IN ANALYZING RESORCINOL & ACETIC ACID SAMPLES
(Samples D14 & D15)

SAMPLE	Reported results as 'Total Phenol"	SYSTEM			
All Samples		Automatic	17 Labs		
		Manual	26 Labs		
D15 Acetic acid	Reported >10µg/L	Automatic	8 (47%)		
		Manual	6 (23%)		
	Reported <= 10µg/L	Automatic	9 (53%)		
		Manual	20 (77%)		
D14 Resorcinol	Reported <3µg/L	Automatic	3 Labs (17.6%)	Temp. =>150°	2 Labs
				Temp. ~143°	1 Lab
				Temp. =<130°	-
		Manual	11 Labs (42.3%)		
	Reported => 50µg/L	Automatic	7 Labs (41.2%)	Temp. =>150°	6 Labs
				Temp.~143°	-
				Temp. =<130°	1 Lab
		Manual	2 Labs (7.7%)		

Note: The percentages expressed in these tables are in terms of either total number of labs with the manual system or total number of labs with the automatic system as the case may be.

The majority of the laboratories (Table 3.3) showed a response less than 10 µg/L. It can be concluded that the majority of the participants will be unbiased by the presence of volatile acids in the sample.

Twelve laboratories (28%) showed a response greater than 10 µg/L (as Total Phenol). These laboratories should evaluate the appropriateness of their buffer system to the type of samples they analyze. Some of the laboratories noted a extremely high off-scale reading which reduced significantly when diluted. In these cases the capacity of the buffer used is sufficient to resist pH changes of samples releasing reduced amounts of acid.

A survey of the buffer systems used by participants in their detection procedure (see Table 3.4) showed that the majority (56%) targeted a pH of 10.0-10.5 for their colour development and measurement. The actual pH in the reaction cell is not known.

TABLE 3.4

Summary of buffer systems used in detection

Target pH	Total number of labs in each pH group	Acetic acid sample (D15) result (µg/L as Total Phenol)	Buffer System				
			Borax/ sod.pot .tartarate	Borax /KCl	Phos-phate	NH_4Cl/ NH_4OH	Other
10 -10.5	23	<=10	-	-	2	11	-
		>10	-	7	1	1	1
9-9.5	10	<=10	8			1	1
		>10	-	-	-	-	-
<9	9	<=10	2	-	4	-	-
		>10	-	-	3	-	-
not reported	1						

Table 3.4 shows that all laboratories using a buffer of pH range of 9.0-9.5 were able to resist changes in pH when analyzing the sample containing Acetic Acid.

Also observed is that all laboratories employing Borax/Sodium Potassium Tartrate system were successful in resisting a pH change when analyzing the Acetic Acid sample. Another interesting feature is that these laboratories (10) showed similar performance in both matrices and that the majority (80%) were assessed as acceptable performers (see table 3.5).

This study suggests that the buffer system consisting of Borax (50 g/L), Sodium Potassium Tartrate (25 g/L) and Acetone (10 mL/L) is the most suitable for the colour development and measurement of Phenolics when interference from volatile acids is possible.

TABLE 3.5

Table of laboratories utilising Borax/Tartrate buffer system

Lab code	pH	Buffer Formula (as provided by participants)	Buffer to sample ratio	Acetic Acid sample result (µG/L as Total Phenol)	Performance Code	
					Reagent Water	Hamilton Harbour Water
3101	9.4	Borax/Sod.Pot. Tartrate	0.12	<2	LI	LI
3103	9.4	50g Borax, 25g Sod.Pot.Tartrate, 10mL acetone/L	0.018	1.5	A	A
3105	9.4	50g Borax, 25g Sod.Pot.Tartrate, 10mL acetone/L	0.16	1.1	A	A
3109	9.4	50g Borax, 25g Sod.Pot.Tartrate, 10mL acetone/L	0.16	2.5	A	A
3118	8.9	39g Borax, 19.5g Sod.Pot.Tartrate, /L	0.12	<0.6	LI	WLS
3122	9.5	50g Borax, 25g Sod.Pot.Tartrate, /L	0.11	1.9	A	A
3132	7.9	Borax	0.19	4	A	A
3140	9.4	50g Borax, /25g Sod.Pot.Tartrate, /L	0.05	<1	A	A
3141	9.2	Borax, Sod.Pot.Tartrate	0.21	4	A	WOC
3143	9.4	Borax, Sod.Pot.Tartrate, Acetone	0.164	1.6	A	A

3.1.2 Resorcinol Sample.

The sample D14 contained 2000 µg/L of Resorcinol ($m\text{-}C_6H_4(OH)_2$).

About one third of the participants did not report any significant amounts of 'Total Phenol' (Table 3.3) for this sample. It can be concluded that about a third of the participants are likely to report 'Non detected' when analyzing samples containing Resorcinol.

29 (67%) of the participants reported Total Phenol content greater than 3 µg/L for the sample containing Resorcinol (D14). Among these 9 reported values greater than 50 µg/L.

Resorcinol has been known to be a difficult 'Phenol' to distil under the usual experimental conditions of the 4-AAP method[6]. As such it is not expected to be recovered under the normal operating conditions of the 4-AAP method. In this study the sample D14 had been deliberately spiked with enormous amounts of Resorcinol and only nine laboratories recovered above 5% of the expected (Based on known response factor for Resorcinol[6]). Some of the laboratories reporting Resorcinol used higher distillation rates/temperature. In as much as they did not recover Acetic Acid, their Phenol results for this sample represent recovery of Resorcinol.

On the one hand manual distillation aims for complete recovery. On the other hand, automated continuous distillation systems are not expected to achieve complete recovery. In this study, however, seven among the nine of the laboratories that reported more than 50 µg/L of 'Total Phenol' used automated continuous distillation system. It is relevant to note that among these seven laboratories, six laboratories also reported significant amounts for the acetic acid sample. This raises an interesting question as to whether the coloured complex measured is indeed a product of Resorcinol and 4-AAP reaction or whether it is a self condensation product of 4-AAP.

It is beyond the scope of this study to investigate the above questions. A closer look into the experimental details of these laboratories will perhaps throw more light.

3.2 HAMILTON HARBOUR WATER SAMPLES

The majority of laboratories (75%) did not find any significant amounts of Phenol (>3 x S_w) in the unspiked Hamilton Harbour water (sample H11). Among the seven laboratories that reported significant amounts of Phenols in this sample, four produced erratic data in the rest of the samples. Another one exhibited similar contamination in unspiked reagent water. Further among these seven, only one laboratory demonstrated acceptable performance in reagent water samples. These observations suggest that Hamilton Harbour water did not contain any significant amounts of Phenols measurable by the 4-AAP method.

The results of the spiked samples H12 and H13 were treated by the K-S procedure. As the matrix was considered as not having any 4-AAP measurable Phenols, spiked samples H12 and H13 were not corrected for blanks.

The outcome of this evaluation is presented in Table 1.1 (page 2), Table 3.2 (page 11) and Figure 3.2.

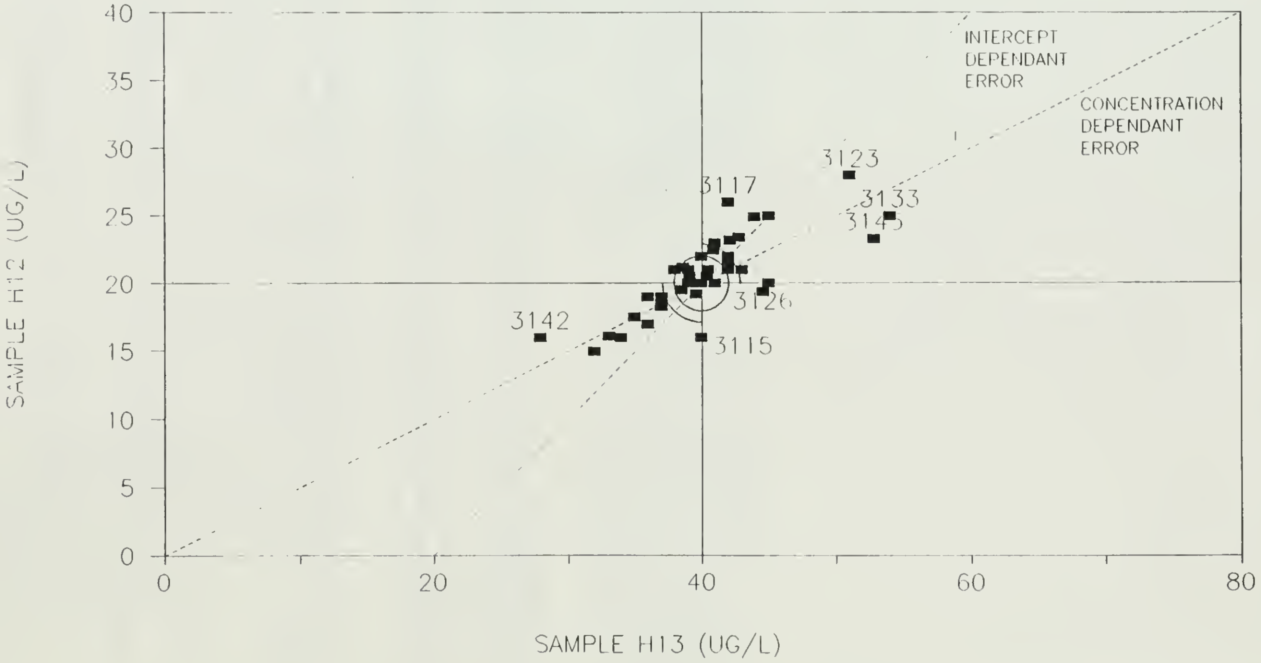
Fifteen laboratories (34.9%) demonstrated acceptable performance. Another eight (total of 23; 53.5%) produced results that were within control limits. This is similar to the outcome of the evaluation of reagent water samples.

The majority of laboratories had similar outcome in both matrices. This includes thirteen laboratories that were assessed as acceptable performers in both matrices. Twenty laboratories (46.5%) were within control limits in both matrices.

FIGURE 3.2

SAMPLE H12 VS H13

HAMILTON HARBOUR WATER



3.3 SUMMARY OF STUDY FINDINGS

- The repeatability estimate of this study is not very different from the previous studies.
- About half the participants are capable of producing valid data in both matrices.
- Nine laboratories have shown improvement in this study compared to the previous studies demonstrating the positive impact of repeated inter-laboratory studies such on data quality.
- The majority of laboratories will not recover Resorcinol (or other similarly less volatile Phenols) under normal operating conditions of the 4-AAP methodology. This reiterates that the 4-AAP method was not intended to measure all Phenolic compounds present in the sample, but rather, provide an minimum estimate of Phenolics present[7]. Presence of compounds such as Resorcinol are not likely to bias the results of the majority of laboratories.
- The presence of volatile acids in the sample are not likely to cause a positive bias for the majority of the laboratories participated in this study. However for laboratories using buffers with insufficient buffer capacity, samples containing volatile acids may cause a problem. This study suggests that Borax/Sodium Potassium Tartrate buffer system is most appropriate for 4-AAP analysis of Phenolic compounds.

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5. APPENDIX

I. EVALUATION METHODOLOGY

Evaluation of the laboratory performance in this study was performed by the King-Selliah[3,4] technique. An outline of this automated spreadsheet-graphical procedure is given below.

I.1 Summary of The Two-Sample Performance Evaluation Procedure

1. Sample distribution-data receipt

   i) Split two samples of different concentrations among a number of laboratories for analysis/measurement using their current methodology.
   ii) Enter data on LOTUS 123® spreadsheet.
   iii) Calculate median (L_m,H_m), means and standard deviations for each sample.
   iv) Tabulate data and return to laboratory analyst for verification.
   v) Correct database if transcription errors were reported.

2. High sample data evaluation:

   i) Reject all results which differ from the median (H_m) by more than 10%
   ii) Calculate median(H), mean and standard deviation (S_h)
   iii) Re-include data if within 3 times S_h
   iv) Re-iterate ii) and iii) until no further data is included
   v) Calculate relative standard deviation of the final selected data (CV_h)

3. Low sample data evaluation:

   i) Use 3 x CV_h x median(L_m) to exclude possible outliers
   ii) Calculate median(L), mean and standard deviation (S_l)
   iii) Reinclude data if within 3 times S_l
   iv) Re-iterate ii) and iii) until no further data is included.

4. Sample data plot format:

   i) Examine the ratio of S_h/S_l and if:
   <2 use data as reported in concentration units
   otherwise convert to % recovery based on expected value if known (otherwise use median values (H,L))
   ii) Prepare paired sample scatter diagrams of all data

5. Performance criteria

i) Calculate perpendicular distance from each point to the two error lines (PD_{slope}, $PD_{intercept}$).
ii) Determine the median (PD_{median}) of all perpendicular distances to the appropriate 45 degree line (intercept error line or slope error line for absolute or relative scale respectively)
iii) Calculate the bias for each laboratory (ie the distance along the appropriate 45 degree line) and if:
<4.5 times PD_{median} select the PD to the 45 degree line other wise select the lesser of the two PDs (PD_{slope} or $PD_{intercept}$)
iv) Determine the median ($PD_{sel-med}$) of selected PDs .
v) Exclude PD values(among previous selection) greater than 2.5 times the $PD(_{sel-med})$.
vi) Determine the median ($PD_{sel-med}$) of remaining PDs.
vii) Re-iterate steps iv) to vi) until $PD(_{sel-med})$ remains unchanged.

6. Set Warning and Control limits

i) Determine the average of all selected PD values less than 2.5 times the $PD(_{sel-med})$ and use this average to estimate the average repeatability S_w (see reference 5)
ii) Set warning limits for repeatability = 2 times S_w
iii) Set control limits for repeatability = 3 times S_w
iv) Set warning limits for possible bias = 3 times S_w
v) Set control limits for possible bias = 4.5 times S_w

6. Code laboratory performance using automated program based on location

i) In upper left or lower right quadrant (erratic)
ii) In lower left or upper right quadrant (biased low or high)
iii) On horizontal or vertical axis (out of control)
iv) On diagonal line through origin (slope or standard problems)
v) On diagonal line not through origin (intercept or blank problems)
vi) Prepare performance assessment table

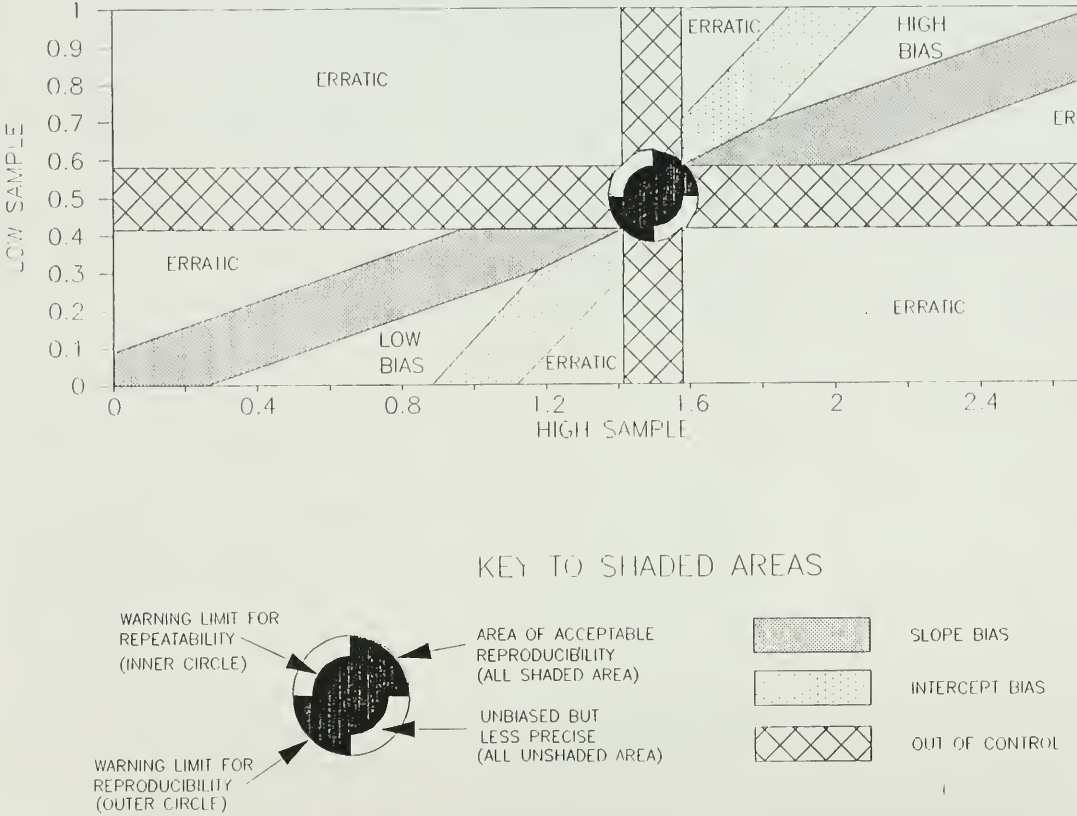
I.2 Limits for Maximum Interlaboratory Repeatability and Reproducibility

The average perpendicular distance (PD) from the bias lines represents the interlaboratory estimate of within laboratory repeatability. It is used to estimate S_w (see Appendix I.1). In some cases the distribution of PD's may suggest two or more levels of laboratory repeatability performance. In such a case the initial median may not represent the central tendency of the data. Therefore an iterative evaluation of the median is included to ensure a stable estimate of repeatability representing a more precise group of participants.

Warning limits and control limits for repeatability are set at $2S_w$ and $3S_w$, respectively. Note that the factors used are somewhat arbitrary but they represent approximately 95% and 99% confidence intervals.

Additional tolerance is required for the effect of variability in preparing and using standards on a day to day or among laboratory basis. But the overall estimate of reproducibility includes data from laboratories with excessive bias. In lieu of this, as a criterion for acceptable reproducibility. S_r is set at 1.5 S_w. Therefore the warning and control limits for reproducibility are set at $3S_w$ and $4.5S_w$ respectively. Based on the F-test a ratio $(S_r/S_w)^2$ exceeding 2.3 (i.e 1.5^2) would be considered significant with a risk of error of less than 10%, 5%, and 1% respectively for 10, 20, and 35 degrees of freedom. Results that exceed warning and control limits determined from this desired maximum interlaboratory (DMI) reproducibility (S_r) are deemed to be possibly or probably biased respectively.

FIGURE 5.0


1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
LOW SAMPLE
0
0.4
0.8
1.2
1.6
2
2.4
2.8
HIGH SAMPLE
ERRATIC
ERRATIC
HIGH BIAS
ERRATIC
ERRATIC
LOW BIAS
ERRATIC
ERRATIC
KEY TO SHADED AREAS
WARNING LIMIT FOR REPEATABILITY (INNER CIRCLE)
WARNING LIMIT FOR REPRODUCIBILITY (OUTER CIRCLE)
AREA OF ACCEPTABLE REPRODUCIBILITY (ALL SHADED AREA)
UNBIASED BUT LESS PRECISE (ALL UNSHADED AREA)
SLOPE BIAS
INTERCEPT BIAS
OUT OF CONTROL

I.3 Two Sample Plot Discussion

This graphical presentation enables all participants to visualize how they have performed compared to others. The assessment of a laboratory in this study is based on the location of its result on the graph. Figure 5.0 identifies the various regions in a typical graph associated with the different types of problems that might be experienced by the participants. Laboratories with controlled repeatability but showing various degrees of bias will appear in the lower left and upper right quadrants. The two circles drawn in this diagram represent the warning limits for repeatability (S_w) and reproducibility (S_r). Those points within the outer circle but in the upper left and lower right quadrants (not shaded in Figure 5.0) are unbiased but somewhat less precise. Those points within the circle but in the upper right and lower left quadrants are precise but acceptably biased. Thus the area of acceptable performance in this diagram has taken the shape of a keyhole.

In a typical graphical presentation such as Figure 3.1, the actual results of each laboratory constitute the points on the graph. The solid lines dividing the graph into four quadrants represent the median results (or targets) of appropriate samples. The 'keyhole' shaped area of acceptable performance, described earlier, is the area de-limited by the inner circle and the outer arcs in the lower left and upper right quadrants. All laboratories that lie outside this area have exceeded the respective warning limits. The two dotted lines are drawn across the graph representing the slope (concentration) dependant error and the intercept (blank) dependant error. The laboratories that exhibit these types of biases will lie along these lines. Some laboratories exceeding warning limits have been identified by their laboratory codes. These laboratories can readily see the nature of their particular problems.

TABLE 5.1
STUDY 92-5 RAW DATA (in µg/L)

SAMPLE	D11	D12	D13	D14	D15	H11	H12	H13
3101	<2	16	36	<2	<2	<2	17	36
3102	<1	17	35	<1	<1	<1	15	32
3103	<0.5	20.0	39.0	3.5	1.5	<0.5	19.5	38.5
3105	0.2, <W	20.0	40.0	4.8	1.1	0.2, <W	20.0	39.6
3106	<100	<100	<100	<100	<100	<100	<100	<100
3107	<2	17	40	<2	<2	<2	21	42
3108	<1	20.5	41.0	87.0	>162	<1	21.0	42.0
3109	<1	20.0	40.0	>100	2.5	1.5	21.0	40.5
3110	<2.0	19.9	39.73	147	113	5.52	24.91	43.98
3111	1.80	21.6	44.2	6.89	ND	1.60	23.4	42.8
3112	0 2	15.2	33.6	1.2	0.2	0.7	16.1	33.1
3113	<2 (<MDL)	19	44	282	>135	<2 (<MDL)	20	45
3115	2	20	36	12	<MDL	<MDL	16	40
3116	1.2	22.0	41.2	7.2	0.0	1.1	21.6	42.0
3117	<2	40	45	8	12	20	26	42
3118	<0.6	17.5	36.8	46.0	<0.6	<0.6	18.3	37.0
3119	7	19	44	<1	<1	<1	21	39
3120	<2	16	36	<2	<2	4	16	34
3121	<2	19	35	3	<2	<2	19	36
3122	<0.5	19.9	39.5	2.7	1.9	<0.5	19.2	39.6
3123	4	10	44	150	0	13	28	51
3124	0.70	21.4	40.3	37.8	123.4	1.70	21.2	38.6
3125	<1.9	20.0	40.0	<1.9	<1.9	<1.9	22.0	40.0
3126	2.5	32.9	46.0	<MDL	7.2	8.7	19.4	44.6
3127	2.0	15.0	42.0	3.0	<1.6	<1.6	17.5	35.0
3128	0.70	20.49	40.45	3.70	11.15	1.47	22.45	40.89
3129	<2	21	39	159	181	<2	21	43
3130	<2	20	37	391	15	2	21	38
3131	20	42	63	33	21	22	44	63
3132	<2	20	38	3	4	<2	20	44
3133	<6	15	42	12	185	49	25	54
3134	<2	22	40	7	123	2	25	45
3135	0.72	20.5	39.1	78.2	2.91	1.45	20.5	39.1
3136	<0.8	21	37	<0.8	<0.8	<0.8	19	37
3137	<2.0	19 5	38.8	190.0	20.0	3.0	22.0	42.0
3138	<2	19	39	13	25	<2	<2	<2
3139	2.34	22.57	41.32	5.30	1.97	2.95	23.18	42.13
3140	<1	20	39	<1	<1	<1	20	39
3141	<2	21	40	399	4	3	23	41
3142	<5	14	33	<5	<5	<5	16	28
3143	0.9	20.5	40.8	3.0	1.6	0.9	20.5	40.4
3144	ND	18	39	47	136	2	20	40
3145	<2.0	21.2	43.1	4.1	<2.0	<2.0	23.3	52.8

III LIST OF PARTICIPANTS

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2 Atomic Energy of Canada, Chalk River
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5 Bondar Clegg & Co., Ottawa
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8 City of Vancouver, Vancouver, B.C.
9 Conestoga-Rovers and Associates, Waterloo
10 Dofasco, Hamilton
11 Domtar Research Centre, Senneville, Quebec
12 Dow Chemical Canada, Sarnia
13 Econotech Services Ltd., New Westminister, B.C.
14 Entech, Kitchener
15 Enviroclean, London
16 Environmental Protection Lab.,Mississauga
17 Esso Petroleum, Nanticoke
18 Esso Petroleum, Sarnia
19 G & S Analytical Laboratory, Toronto
20 Lab Elite Ltd., Montreal, Que.
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22 Mann Testing Laboratories, Mississauga
23 Ontario Hydro, Toronto
24 Ontario Ministry of the Environment, London
25 Ontario Ministry of the Environment, Rexdale
26 Ontario Ministry of the Environment, Rexdale
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29 Petro Canada Ltd., Mississauga
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33 Regional Municipality of Hamilton- Wentworth
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37 Stelco Steel, Nanticoke

38 Sunoco Inc., Sarnia

39 Technical Services Laboratory, Mississuga

40 Walker Laboratories, Thorold

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